



Geochemistry of sediment moisture in the Badain Jaran desert: Implications of recent environmental changes and water-rock interaction



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ABSTRACT

Unsaturated zone pore water has the potential to record history of recharge, palaeoenvironment, pollution movement and water-rock interaction as it percolates through and moves towards the water table. In this study, two 6-m cores from the Badain Jaran desert (NW China) were collected to explore this potential using directly extracted moisture. Pore waters in these unsaturated zone sediments (1–5% moisture by wet weight) were directly extracted using immiscible liquid displacement and then analysed for major anions, cations and trace elements. Results show enrichment in pore water chemistry in the top 1–2 m where strong temperature and moisture fluxes occur. The enrichment in cations relative to chloride is primarily due to silicate mineral dissolution during infiltration. High nitrate and low iron concentrations indicate the overall oxidizing environment, which allows the mobility of oxyanions, such as uranium, arsenic and chromium. The trace elements show enrichment in the upper zone of fluctuation where chemical gradients are strong, but with lesser reaction lower in the profile. The calculated groundwater recharge rates using the chloride mass balance are negligible in this arid region between 1.5 and 3.0 mm/year. The modern rainfall infiltration signature contrasts with that of the underlying groundwater body, which has a distant, regional recharge signature.

This reconnaissance study demonstrates the potential for a new geochemical approach to studying geochemical processes in the unsaturated sediments in semi-arid environments due to both natural and human influences. The use of directly extracted water, rather than extraction by dilution (elutriation), facilitates an improved understanding of hydrological and geochemical processes in the unsaturated zone and into the capillary fringe at the water table, because it avoids potential chemical changes induced during elutriation.

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1. Introduction

Rainfall entering the soil moves through the unsaturated zone (USZ) before recharging groundwater. Geochemical profiles of recharging moisture within the USZ have a range of potential applications i) to enable estimation of groundwater recharge rates; ii) to retain information related to antecedent climatic hydrological and land use conditions; iii) to investigate pollution in transit to the

water table, which provides information for source protection and iv) to provide a record of water-rock interaction and solute acquisition for potable and other uses. In view of the low moisture contents most previous studies have relied mainly on moisture extraction by dilution (elutriation) using demineralized water. The use of chloride mass balance (CMB) as a tool for estimating recharge in unsaturated porous mainly sandy profiles has now become a standard procedure in hydrogeology especially in semi-arid regions (Edmunds et al., 1987; Allison et al., 1994; Scanlon et al., 2006). Moreover the recharge records so obtained are generally robust, providing estimates over decades or longer periods. Under favourable conditions, especially in areas with deep USZs, the chloride (Cl) record can act as a proxy of past climatic conditions

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(Edmunds et al., 1991; Scanlon, 1991; Edmunds and Tyler, 2002). Recent records from low rainfall areas of Inner Mongolia, China have provided an archive over 2000 years in USZs of up to 30 m which can be validated against other proxies such as ice cores, tree ring and historical records (Gates et al., 2008a; Ma et al., 2009).

The USZ has also been used extensively in geochemical studies of water quality evolution over decadal timescales using moisture extracting via either elutriation or centrifugation techniques (Edmunds and Bath, 1976). The USZ (as well as saturated zone) profile studies have now become standard procedures for investigating penetration of pollution from agricultural sources such as, agrichemicals and pesticides (Geake and Foster, 1989) and from industrial sources such as landfill (Williams et al., 1991). Centrifugation of USZ porous media however becomes limiting with moisture contents lower than around 8–10%.

Direct investigation of the geochemistry of the USZ at low moisture contents (2–6%) has proved to be a challenging problem. Investigation of inert solutes such as Cl and nitrate (NO₃) under aerobic conditions can be achieved by dilution methods, but investigation of wider geochemical applications requires direct access to the pore solution so as to avoid artifacts from washing off particle coatings and changing the chemical conditions of moisture created by the dilution process. An immiscible displacement method was developed in the 1980s (Kinniburgh and Miles, 1983) using the chlorofluorocarbon Arklone which allowed between 30 and 60% recovery of moisture. This technique was then successfully applied to studies of acid attenuation in the USZ where typically between 2 and 4 ml moisture was used for investigation of exchangeable cations (Moss and Edmunds, 1992). This promising technique was however brought to an abrupt halt by the Montreal Protocol which led to a phasing out and a halt to production of CFCs. Until recently no suitable substitute for Arklone had been found.

A new immiscible liquid (HFE-7100[®]) has however now been successfully trialled (Jin and Edmunds, 2010) and this paper is the first field application of the technique in the research area for which it was designed. The objective of this paper is to investigate the potential of the method for studying directly the USZ moisture geochemistry in an arid region of China (the Badain Jaran Desert) where previous work on the CMB and recharge history has been carried out (e.g. Gates et al., 2008b; Ma et al., 2009). The paper presents the empirical relationships between major ions and key trace elements. This is a reconnaissance study to demonstrate the potential of a new geochemical approach rather than a study of detailed processes.

2. Materials and methods

2.1. Study area

The Badain Jaran desert, located in Northwest China, is a remote region of massive sand dunes with the relative height being 200–500 m above sea level and numerous lakes with diverse composition, from fresh to saline (Fig. 1). It is the second largest desert in China with an area of 49,000 km². The Badain Jaran desert is surrounded by the Heishantou and Yabulai mountains to the south and southeast, respectively; the lowland areas of the Gurinai grassland lie to the west and northwest (Fig. 1). Two sites on the southeast side of the Badain Jaran desert were selected for sampling. The first site, Sayinwusu (abbreviated as SS), is located at 39°34′32.1″ N; 102°20′17.5″ E. Second site, Baoritaolegai (BA), is located at 39°36′22.2″ N; 102°28′54.8″ E.

Badain Jaran desert is located in the basin depression of the Alxa platform (Ma and Edmunds, 2006). The center of the basin is occupied by Quaternary sediments (Ma and Edmunds, 2006). The fringe of the basin is surrounded by Jurassic, Cretaceous and

Tertiary age rocks. The Pleistocene sediments are mostly fine-grained or clayey fluvial and lacustrine origin (Cai, 1986). The Holocene Aeolian sands are deposited above these older sediments and form the dominant desert landscape. The sediments are dominated with mineral quartz with occasional iron coatings and some feldspars.

The desert landscape mainly consists of sparsely vegetated aeolian sand dunes. The interdune areas often contain groundwater-fed lakes and playas, which vary widely in surface area and salinity (Yang and Williams, 2003). The strong continental climate in the Badain Jaran gives mean monthly temperatures from ~–10 °C in January to ~25 °C in July. In summer months the diurnal temperatures range from ~0 to >40 °C (Gates et al., 2008b). About 70% of precipitation falls from July to September, strongly influenced by the Asian monsoon. The mean annual precipitation measured at Zhongqanzi Station (~20 km southeast of the study area) was 84 mm from 1956 to 1999, although it is highly variable (standard deviation 33 mm/yr). The potential evaporation is approximately 2600 mm/yr (Gates et al., 2008b). The major shallow aquifer in the Badain Jaran desert consists of Quaternary sediments, occurring at shallow depth and the water table reaches the surface as lakes in many inter-dune areas. Lacustrine sediments with low porosity may provide local confining layers (Gates et al., 2008b).

2.2. Sampling and methodology

2.2.1. Sample collection

The unsaturated sediments of the USZ were sampled using a hollow-stem hand auger (Dormer Engineering, Murwillumbah South, NSW, Australia) with interchangeable 1.5 m aluminium rods. Two profiles to approximately 6 m depth were obtained, with samples taken at intervals of 12.5–25 cm. Any carryover of sediment from overlying material was usually visible as a colour change at the top of the sample interval and discarded. Samples were rapidly homogenized in plastic bags shortly before transferring to sealed jars to avoid moisture loss.

2.2.2. Rainfall

No rainfall sampling was possible for this study period, neither has there been any regular local monitoring of solute concentrations in rainfall. However, Ma and Edmunds (2006) reported Cl concentration of 1.49 mg/l from a large storm (50 mm that consisted of the majority of the annual rainfall) in the Badain Jaran desert in 1999. Subsequent sampling from Zhongqanzi station during 2001–2002 had a volume weighted mean Cl of 1.5 mg/l (Ma and Edmunds, 2006). Cl concentrations from 10 storm events in the Badain Jaran during 1994–1995 ranged from 0.5 to 3.3 mg/l (Hofmann, 1999) with a simple arithmetic mean of 1.9 mg/l. In this paper, we chose the value of 1.5 mg/l as the best available estimate for Cl concentration in the rainfall in the area. The rainfall input data for all elements used in this paper are given in Table 1.

2.2.3. Moisture content and water extraction

Moisture contents were determined on 50 g samples on a wet weight basis, before and after drying overnight at 105 °C. The moisture contents were then calculated according to the mass difference. The balance is precise down to 0.01 g, sufficient to detect moisture content changes as low as 0.02%.

Approximately 100 g of individual moist sand sample was loaded into 250-ml polypropylene centrifuge bottles. The bottles were thoroughly cleaned and rinsed with deionized water before use, and 230 g of immiscible liquid (HFE-7100) was added. Each sample was centrifuged for 1 h at a speed of 13,000 rpm (2.3 MPa) in a Beckman J2-21 centrifuge with JA-14 fixed angle rotor (Jin and Edmunds, 2010). After centrifuging, the displaced water collected

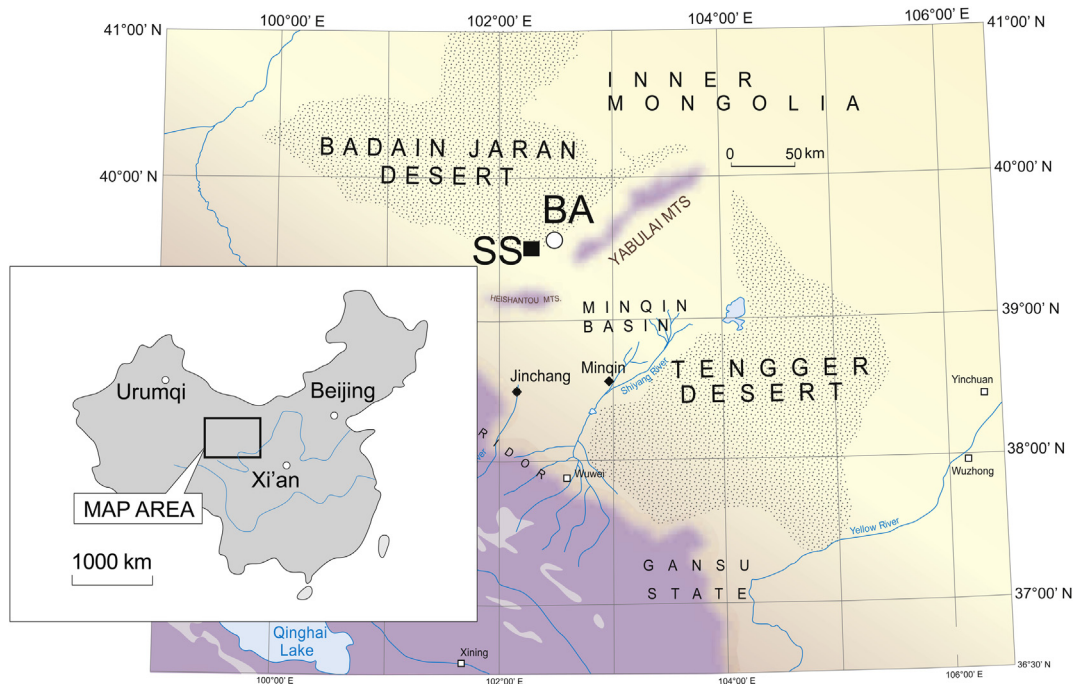


Fig. 1. A site map of two sediment cores (BA and SS) collected in the Badain Jaran Desert in Northwest China.

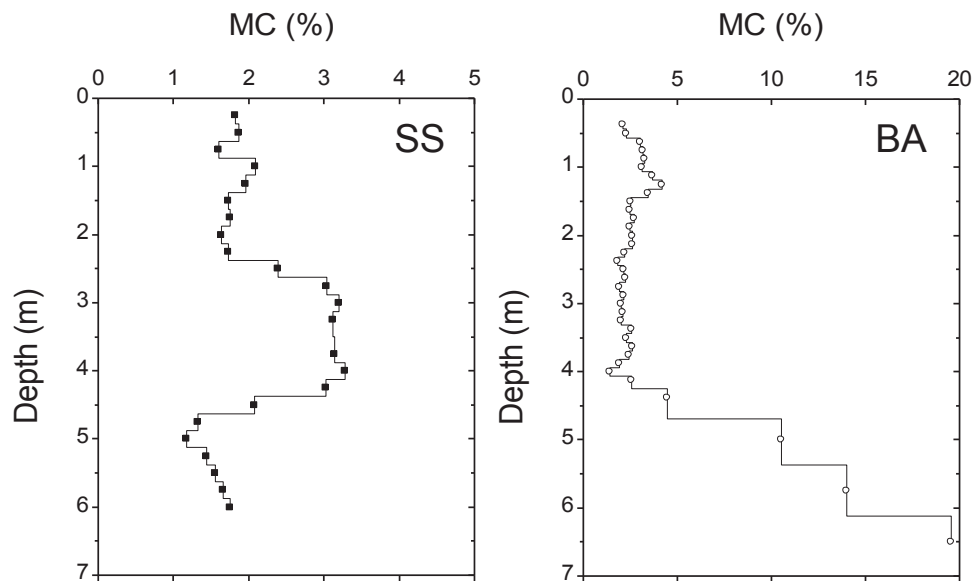


Fig. 2. Moisture content profiles of SS and BA.

as a small meniscus above the immiscible liquid and was withdrawn using a micro-pipette. The displaced water was transferred to a pre-weighed 10-ml clean vial. Full details of the immiscible displacement technique are given in Jin and Edmunds (2010). The average moisture yields were 2 ml, representing approximately 30% of the moisture. These samples were then diluted according to yields to provide 10 ml of water for chemical analysis.

2.2.4. Chemical analyses

pH was measured on 20 g field moist samples, on return to the laboratory, to which 5 ml CaCl_2 solution water was added (ASA, 1982).

The moisture extracts were analysed for major cations, anions and a suite of trace metals. Anions (F, Br, Cl, NO_3 , and SO_4) were analysed using an ion chromatography (DX-500 Ion Chromatograph, Dionex Corp., Sunnyvale, CA), equipped with an AS14 3.5 mM Na_2CO_3 /1.0 mM NaHCO_3 eluent column, and an AS50 autosampler. Internal standards (Aquacheck Scheme) were analysed and checked at the beginning and end of each run, and a blank and 3 standards were analysed every 10 samples for quality assurance and quality control purposes. Detection limits for anions F, Br, Cl, NO_3 , and SO_4 are 0.05, 0.01, 1, 1, 3, respectively (units in mg/l), not allowing for dilution of pore moisture samples. Analytical precision is within 5% based on the reproducibility of 1 mg/l

Table 1

Precipitation analysis in Baoritelegai, the Badain Jaran Desert (after Ma and Edmunds, 2006), which is used as rainfall input data in this paper.

	Concentrations (mg/L)
pH (field)	7.85
Cl	1.49
SO ₄	4
HCO ₃	8.1
NO ₃	0.58
Na	2.5
K	0.9
Ca	2.14
Mg	0.22
Br	<0.02
F	0.01
Si	<0.07
Ba	0.002
B	<0.2
Li	<0.009
Fe	0.05
Mn	0.009
Sr	0.011
Al	0.014
Zn	0.013

standards. Bicarbonate could not be measured on the low volumes and the only option has been to determine by difference, the anion deficiency in the ionic balance.

Cations (Ca, Mg, Na, K, and Sr) and trace metals were analysed using inductively coupled plasma mass spectrometry (ICP-MS). The extracted waters were diluted between 6 and 50 times for the analysis (with resultant lowered effective detection limits). The following elements were used in the study: Rb, Sr, Ba, Cr, Mo, As and U. Other trace elements including Li, Be, B, Al, Ti, V, Mn, Fe, Co, Cu, Ni, Zn, Ga, Se, Y, Zr, Nb, Ag, Cd, Sn, Sb, Cs, La series, Lu, Hf, Ta, W, Tl, Pb and Th were measured but were below the instrumental 3-sigma detection limit.

2.2.5. Recharge rates and residence time calculation

The USZ recharge rates were calculated based on the CMB, developed by Allison and Hughes (1978) and Edmunds and Walton (1980) and now widely adopted (Scanlon et al., 2006). This method relies on the conservative behaviour of Cl and the fact that deep USZs contain robust long term recharge records at decadal scale or longer. The approach considers the balance of the Cl mass between rainwater and the USZ where Cl is enriched as a result of evapotranspiration. This mass balance can be written as:

$$P \times C_p = R \times C_R \quad (1)$$

where P is the precipitation amount, C_p is the Cl concentration in rainwater, R is the recharge rate, and C_R is the mean Cl concentration of pore waters (Edmunds et al., 1988). It is generally assumed that dry deposition as aerosols is in steady-state with the land surface. Recharge is then proportional to 1/Cl.

Assuming all the Cl is derived from atmospheric precipitation and assuming piston flow, the residence time of pore moisture can be estimated from the accumulation of Cl in the USZ using the following equation:

$$t = \frac{1}{P \times C_p} \int_0^z \theta(z) C_R(z) dz \quad (2)$$

where t is the residence time, θ is moisture content and z represents the depth (Tyler et al., 1996).

3. Results

All element data are both graphically and numerically summarised in Table 2 where the data are grouped according to depth interval for the USZ of each profile. These results are then compared to regional groundwater from the same area, using an average of the older underlying unconfined groundwater body. In the plots of element concentrations, or element molar (m) ratios, with depth (Figs. 3–9) values below detection limits are omitted.

3.1. Moisture content and pH

The unsaturated sediments of the Badain Jaran desert consist mainly of well-sorted fine sands with occasional layers of silt and lacustrine deposits, and have moisture contents between 1% and 5% at both sites (Fig. 2), falling in the same range reported by previous studies in this area (Gates et al., 2008b). Oscillations in moisture content correlate with the clay fraction of the sediment. The moisture content within BA starts to rise below 4 m reaching 20% at the base of the profile, indicating a content close to saturation (~21% for dry sand) and representing a 2 m capillary fringe above the water table. There is a small peak of relatively high moisture reaching 4.2% at 1.25 m, compared to the baseline around 2%. Profile SS did not reach the water table which was estimated to be at 10 m below the sampled intervals (Gates et al., 2008b). A broadly defined peak was found between 2.5 and 5 m in SS, related to a finer-grained region of the sedimentary profile.

pH values of extracted moisture are alkaline (8.5–9.5). As direct measurements were not possible due to the sampling method and/or volumes obtained using direct extraction, caution is required in equating these measurement with field conditions.

3.2. Anion profiles

The Cl concentrations are considered first and then other anions are discussed in relation to the Cl, which is later used as a reference element. In the following plots the rainfall values (R) are indicated (see Table 1 for elemental concentrations in rainfall). At site BA, all anion species show considerable down-profile variations in concentration (Fig. 3). The top 1–2 m lie in a zone of strong temperature and moisture flux often referred to as the zone of fluctuation (Wellings and Bell, 1980), where solutes become concentrated due to evapotranspiration and where occluded pockets of mineralization may develop if mineral saturation is reached. Cl enriched pore fluids may also become trapped as fluid inclusions during mineral formation (eg carbonate). Below the zone of fluctuation water percolates to the water table together with the modified/concentrated input signatures. The SS profile shows a near surface Cl peak but in the BA profile, the near-surface peak is absent (Fig. 3 ai and Fig. 4 ai).

Two significant Cl features are clearly visible in the BA profile above a baseline around 20–30 mg/l (Fig. 3 ai). There is a peak of Cl concentration, between 1 and 2 m, with the highest value above 100 mg/l. Below 4–5 m, the Cl concentration rapidly increases with depth, reaching 329 mg/l at the base of the profile. The upper peak is related to present-day input variations but the lower peak corresponds with the capillary zone and the water table with a significantly higher salinity. This is consistent with previous work at this site where it has been shown that the groundwater feeding the lake at BA is much older regional groundwater recharged from the Yabulai Mountains (30 km to the southeast, Fig. 1) and of different chemistry to the present day recharge (Ma and Edmunds, 2006; Gates et al., 2008b). The SS profile has Cl concentrations which range from 20 to 130 mg/l below the surface peak (Fig. 4 ai) without a capillary fringe region.

Table 2
Summary of all major and trace element concentrations (Gates data are from Gates et al., 2008d).

	Major cations					Major anions					
	Ca	Mg	Na	K	Si	SO ₄	Cl	NO ₃	Br	F	(calc) HCO ₃
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
BA Jin USZ (to 4 m)	53	14	41	9.1	6.8	103	40	47	0.11	0.29	105
BA Jin USZ (5–5.75 m)	25	24	112	13	6.1	109	64	77	0.16	9.9	160
BA Jin WT (at 6.5 m)	50	29	317	17	4.8	337	329	18	0.36	5.4	135
BD Gates GW (1, 3, 4, 5, 7)	50	26	181	16	n.a.	166	154	63	n.a.	n.a.	201
SS Jin USZ (to 6 m)	80	22	81	8.1	7.6	134	88	67	0.12	0.27	191
SS Gates GW	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

	Trace elements									
	Rb	Sr	Ba	Cr	Mo	As	U	Mn	Zn	Sb
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
BA Jin USZ (to 4 m)	4.5	427	23	8.8	8.7	7.7	1.7	53	396	3.5
BA Jin USZ (5–5.75 m)	4.4	712	49	8.5	35	n.a.	13	n.a.	n.a.	n.a.
BA Jin WT (at 6.5 m)	2.3	1060	47	2.5	27	n.a.	11	n.a.	n.a.	n.a.
BD Gates GW (1, 3, 4, 5, 7)	3.0	136	4.7	2.6	5.0	1.0	1.0	n.a.	5.8	0.57
SS Jin USZ (to 6 m)	3.6	650	21	6.3	6.5	8.8	6.0	24	464	0.60
SS Gates GW	0.25	292	3.0	1.3	4.7	0.98	5.9	n.a.	0.0	0.01

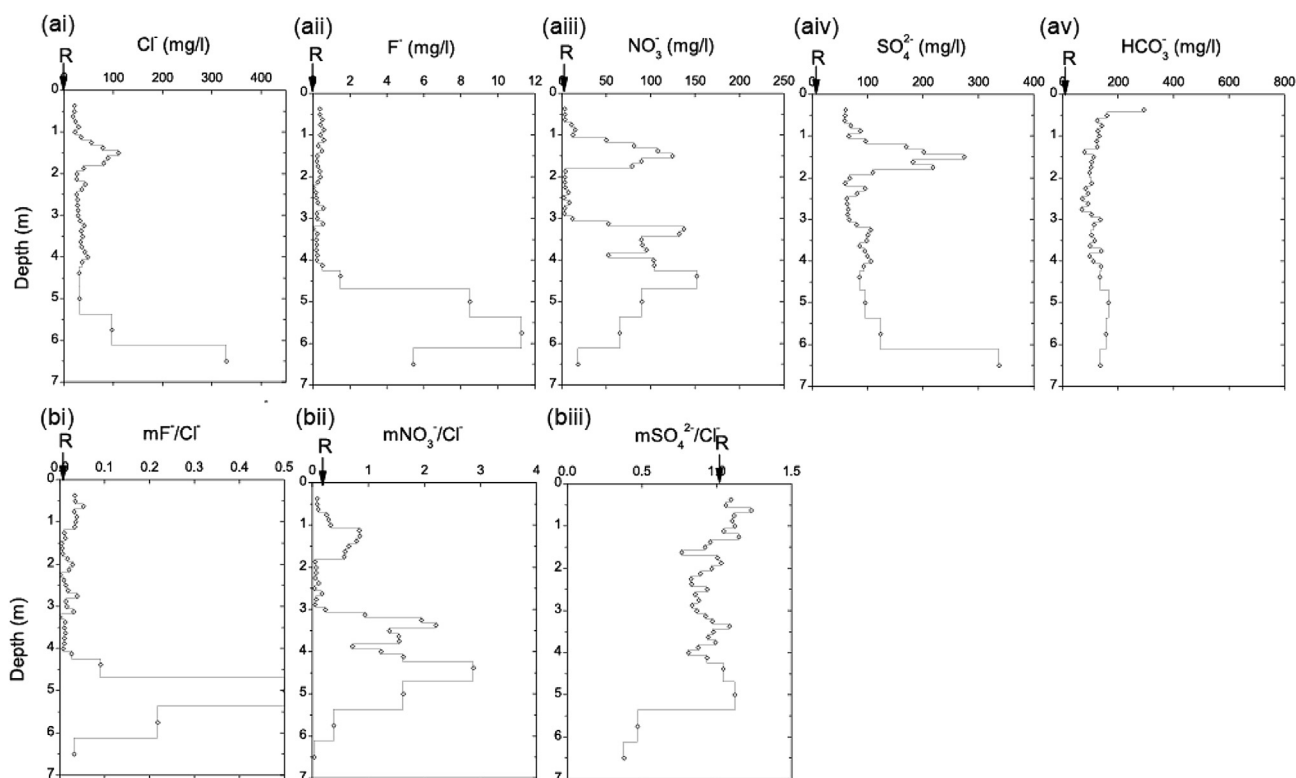


Fig. 3. Major anion concentrations of BA profile (ai to av) and major anion to Cl molar ratios of BA profile (bi to biii). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

Bromide and the ratio mBr/Cl can be used to help constrain the source of the Cl (Edmunds, 1996; Davis et al., 1998). The mBr/Cl ratio in sea water is 0.0156 and maritime rainfall is slightly enriched due to the higher Br in sea surface aerosols; however there is then preferential rainout of Br over the continents (Winchester and Duce, 1967). The average ratio mBr/Cl in the profiles is 0.0088, consistent with a Cl source depleted in Br, yet this value is not as low (0.0032) as in groundwater (with higher Cl) below the sampled USZ profiles (Table 2). This suggests the presence of the regional groundwater in this zone, which has

stronger evaporite signature and a different source compared to the USZ.

The USZ F concentrations in both profiles are in the range 0.1–0.5 mg/l (Fig. 3 aii and Fig. 4 aii) and no evidence is found of enrichment during percolation, these concentrations being consistent with evaporative concentration of rainfall (Table 1). At the base of profile BA, F concentrations then increase sharply in the capillary zone and into the saturated zone to around 10 mg/l (Fig. 3 aii), which again provides strong evidence for the different origin of the regional groundwater (Gates et al., 2008b). The

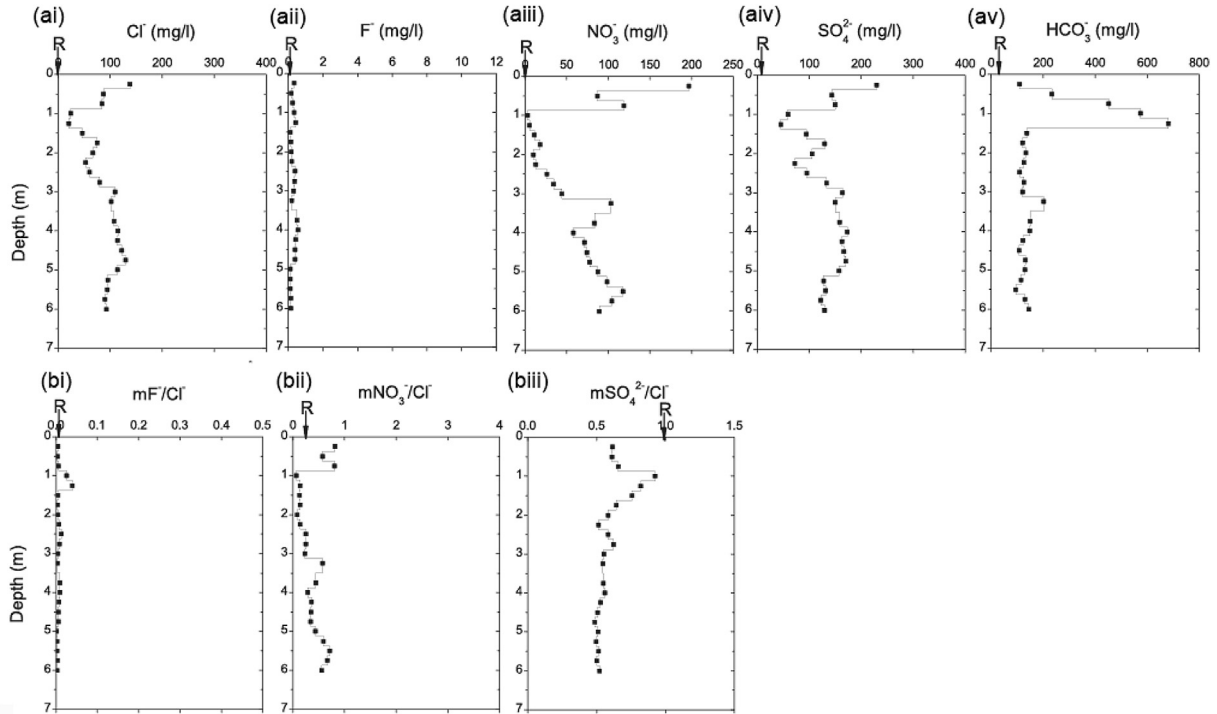


Fig. 4. Major anion concentrations of SS profile (ai to av) and major anions to Cl molar ratios of SS profile (bi to biii). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

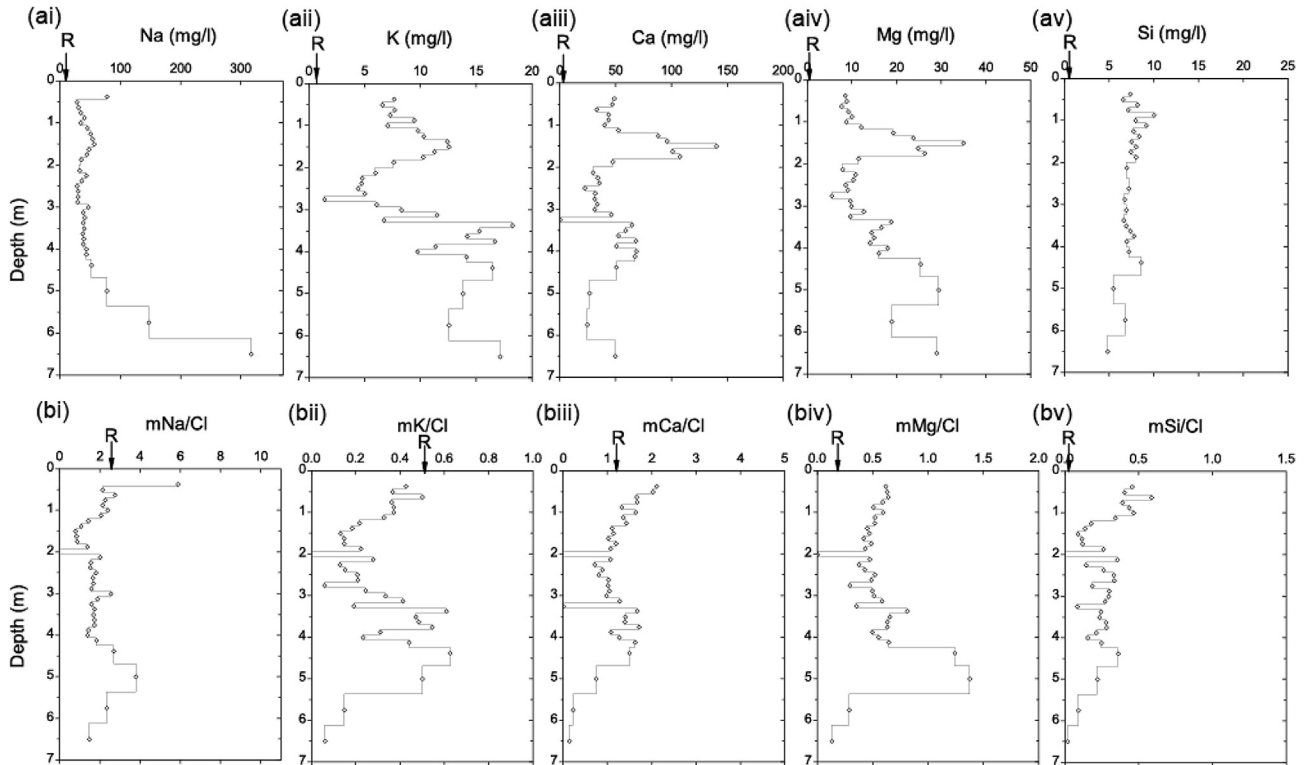


Fig. 5. Major cation concentrations of BA profile (ai to av) and major cations to Cl molar ratios of BA profile (bi to bv). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

increase in mF/Cl at the water table (Fig. 3 bi) combined with the anomalously high values confirms that the F increase is not just salinity related but must be due to water-rock interaction along the line of flow over long residence times (Gates et al., 2008b; Ma

and Edmunds, 2006).

The NO_3^- profiles are more complex than for the other anions (the patterns of behaviour suggest a control independent from other ions) but are generally enriched over atmospheric levels

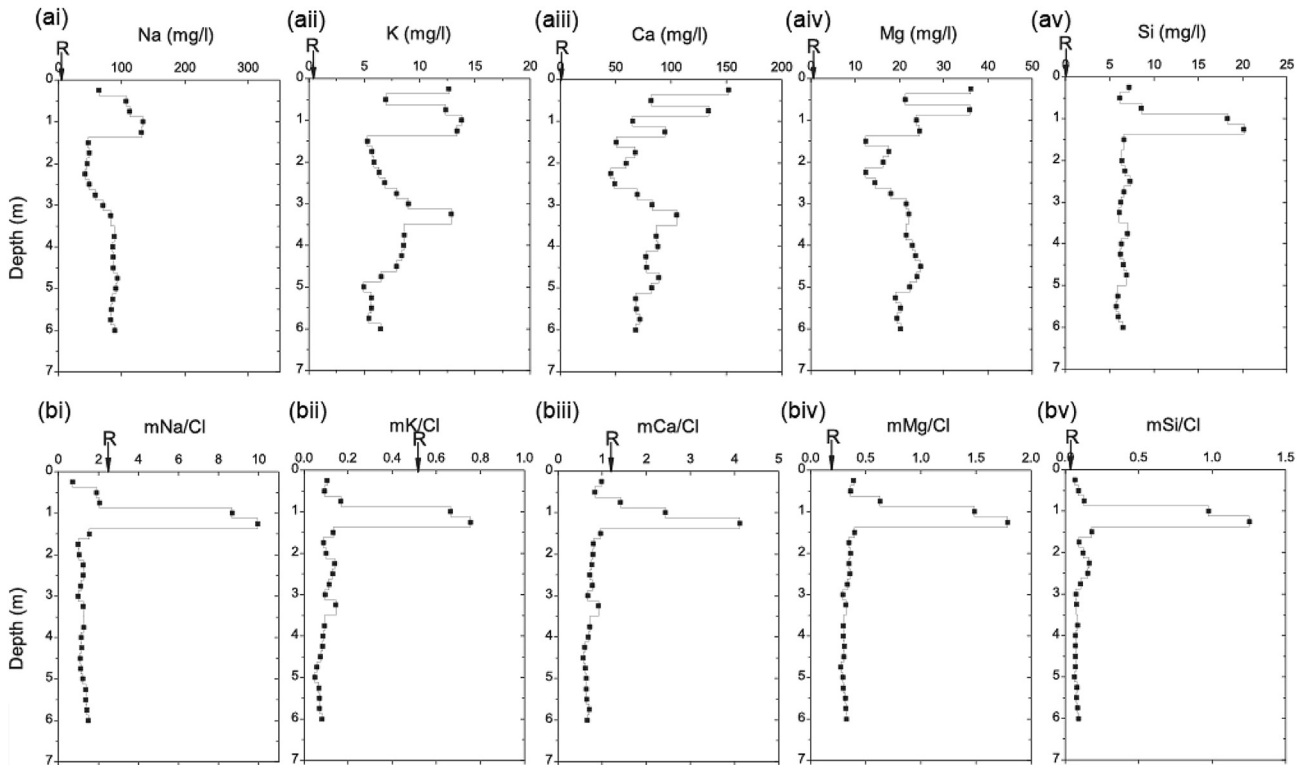


Fig. 6. Major cation concentrations of SS profile (ai to av) and major cations to Cl molar ratios of SS profile (bi to bv). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

(Fig. 3 aiii and Fig. 4 aiii). In profile BA there are two distinct peaks (100–150 mg/l NO_3) at 1.5 m and 3.25 m depths (Fig. 3 aiii). From the Cl profile the influence of the capillary fringe/water table lies below 5.5 m and therefore the USZ profile data suggests the NO_3 concentration at/near the water table is around 20 mg/l, consistent with the oxidizing conditions found in the regional aquifer (Gates et al., 2008c). The oscillating and high NO_3 concentrations are considered to indicate enrichment by intermittent biological process in the soil zone. Similar levels of N enrichment and variation are seen in SS profile which has a near surface maximum near 200 mg/l NO_3 and with low values around 2–3 m (Fig. 4 aiii). High concentration peaks of 100–150 mg/l NO_3 occur in both SS and BA profiles. In the USZ of profile BA, mNO_3/Cl values reach 2.5–3 with minima close to a baseline similar to that of the single value for rainfall (0.22) (Fig. 3 bii and Table 1). In contrast, mNO_3/Cl in profile SS mostly remains close to the rainfall value with an enrichment in the top 1 m and 5–6 m (Fig. 4 bii). Our results compare with those from Gates et al. (2008c) who found high mNO_3/Cl ratios in USZ moisture (mean 0.89 and range 0.03–2.92).

In profile BA the SO_4 mirrors closely the behaviour of Cl (Fig. 3 aiv). The equimolar mSO_4/Cl ratios in the capillary and saturated zones (above 5.5 m) (Fig. 3 biii) are comparable to rainfall (Ma and Edmunds, 2006, Table 1). The groundwater mSO_4/Cl ratio (0.4) is lower than in the unsaturated profile again emphasising the different water origins (Fig. 3 biii and Table 2). Profile SS in contrast has a lower mean profile ratio mSO_4/Cl (0.5), lower than rainfall and there is a peak of SO_4 at 1 m depth ($\text{mSO}_4/\text{Cl} = 1.0$) with a dispersion front to a depth of 2.0 m (Fig. 4 biii).

Alkalinity was measured by the ionic balance and gave consistent results. In both profiles the alkalinity (as HCO_3) shows contrasting concentrations in the zone of fluctuation but uniform concentrations (100–150 mg/l) in upper sections of both profiles

(Fig. 3 av and Fig. 4 av). In profile SS concentrations reach 600 mg/l in the zone of fluctuation (with corresponding high Ca) (Fig. 4 av).

3.3. Major cations and silicon

The major cations (Na, K, Ca and Mg) and silicon are shown as depth profiles and as selected ratio plots (using Cl as a reference to show any changes in reactive solutes over and above controls on salinity) (Figs. 5 and 6). The ratio mNa/Cl (mean of 1.5–2 in both profiles) confirms a net increase in Na with depth indicating the likely addition in this environment from silicate mineral dissolution (Fig. 5 bi and Fig. 6 bi). A major exception is the anomaly at 1 m depth of profile SS, where mNa/Cl is enriched corresponding with an interval with low Cl concentrations (Fig. 6 bi and Fig. 4 ai). Increasing Na through mixing with the more saline regional groundwater is seen at the base of profile BA (Fig. 5 ai), although the mNa/Cl ratio remains similar as rainfall input (Fig. 5 bi and Table 1).

Potassium concentrations mirror Na concentrations, and there is a slight decrease in mK/Na with depth in profile SS (Fig. 7a). The ratio mK/Na in profile BA is higher than in SS (0.1–0.3 as compared with 0.05–0.1 in the former (Fig. 7a and c). Near the water table the BA pore water has a lower mK/Na ratio (<0.1) corresponding to the saturated zone (Fig. 7c).

Calcium shows significant enrichment in the upper 2 m of both profiles and the mCa/Cl below the zone of fluctuation is fairly uniform around 1.0 (Fig. 5 aiii, biii and Fig. 6 aiii and biii). In profile SS, the sharp increase in mCa/Cl (as well as other cations) in the zone of fluctuation at around 1 m depth indicates that silicate weathering reactions must be taking place independent of the salinity (Cl). HCO_3 also shows strongest increase in this zone (Fig. 4 av). The mMg/Ca ratio in profile SS shows a very small enrichment down the profile and a similar trend is seen in profile BA, although values remain slightly below 0.5 (Fig. 7b and d). The regional

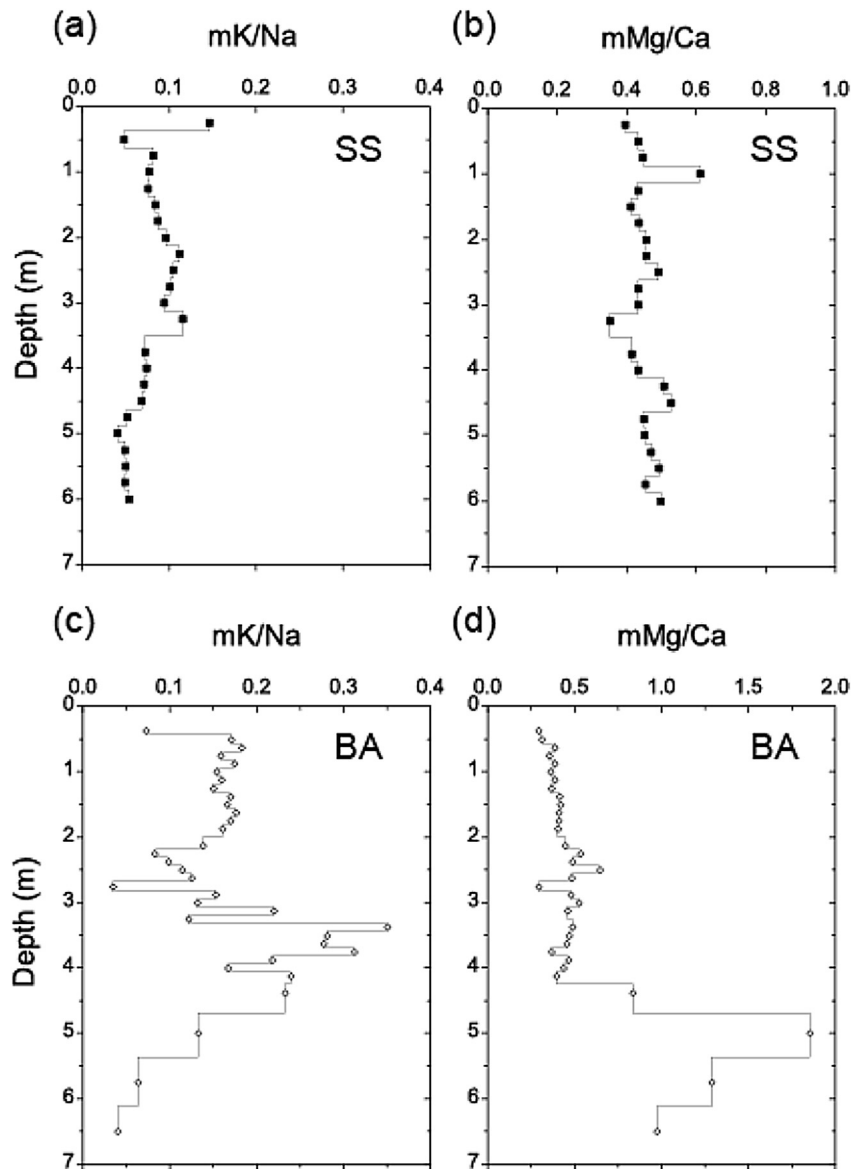


Fig. 7. Cation molar ratios of SS and BA profiles.

groundwater and the capillary zone have a significantly higher mMg/Ca (1.0–1.5) (Fig. 7d and Table 2).

Silicon (Si) concentrations are high (above 5 mg/l) in near surface horizons and continuing to depth in both profiles with concentrations averaging 6 mg/l (Fig. 5 av and Fig. 6 av). This uniform enrichment in Si is the result of weathering of the most soluble primary silicates, notably feldspar (Berner and Holdren, 1979) and under the alkaline conditions the Si will exist as H_4SiO_4 buffered by amorphous Si solubility. The only anomaly is a distinct enrichment in profile SS at 1 m depth where Si is enriched to 20 mg/l which correlates with higher Na and K concentrations consistent with the weathering of feldspars (Fig. 6 av).

In summary, the major ions in the USZ profiles show enrichment in cations versus the reference element Cl at 1–2 m depth demonstrating reaction of silicate minerals during percolation and this is mirrored by pore water Si concentrations. The groundwater of higher cation concentrations at the water table and a transitional capillary zone of up to 2 m is geochemically distinct indicating a different origin compared to the modern infiltration.

3.4. Trace elements

The following elements found at concentrations significantly above the 3-sigma detection limits are used to support and develop the geochemical interpretation: Rb, Sr, Ba, Cr, Mo, As and U. Profiles are plotted in Figs. 8 and 9 and have also been plotted normalized to Cl to emphasise where water-rock interaction is distinct from evaporative enrichment. Both profiles have concentrations well above detection indicating that water-rock interaction must be very rapid in this environment where sharp changes in moisture content, temperature and chemical gradients occur.

In profile BA, Rb concentrations range between 2 and 6 $\mu\text{g/l}$ in the USZ and decreased to background level at the capillary zone (Fig. 8 ai). Rb shows variations relative to salinity which closely follow those for K (Fig. 5 bii and Fig. 9 ai). The ratio $Rb \times 1000/K$ in profile BA is 0.48 (plot not shown). This is enriched (in the absence of rainfall data) versus the sea water average (0.31) consistent with the continental weathering environment and compares also with the K/Na ratio (0.22) relative to the marine average of 0.03 (Hem,

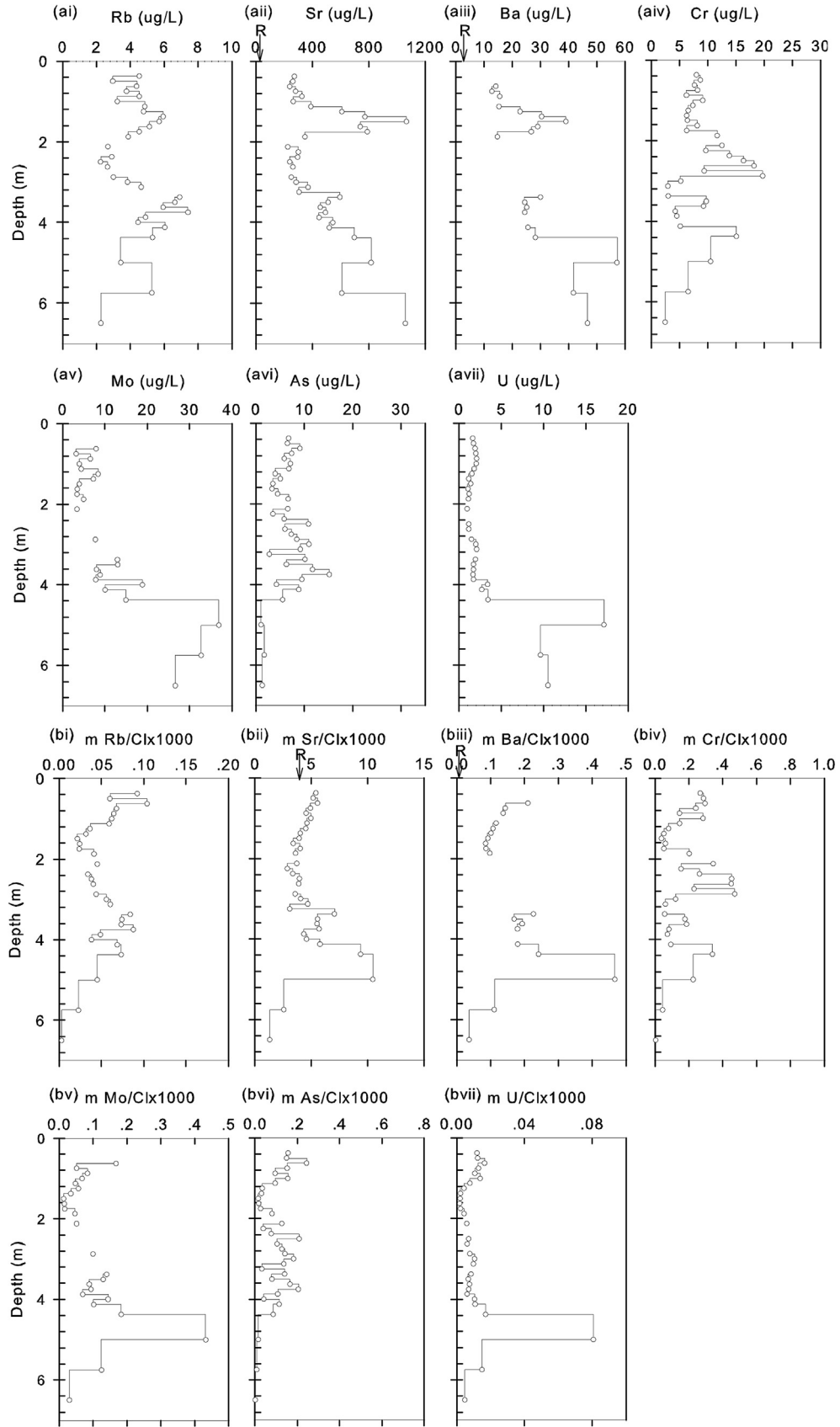


Fig. 8. Trace element concentrations of BA profile (ai to avii) and trace element to Cl molar ratios of BA profile (bi to bvii). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

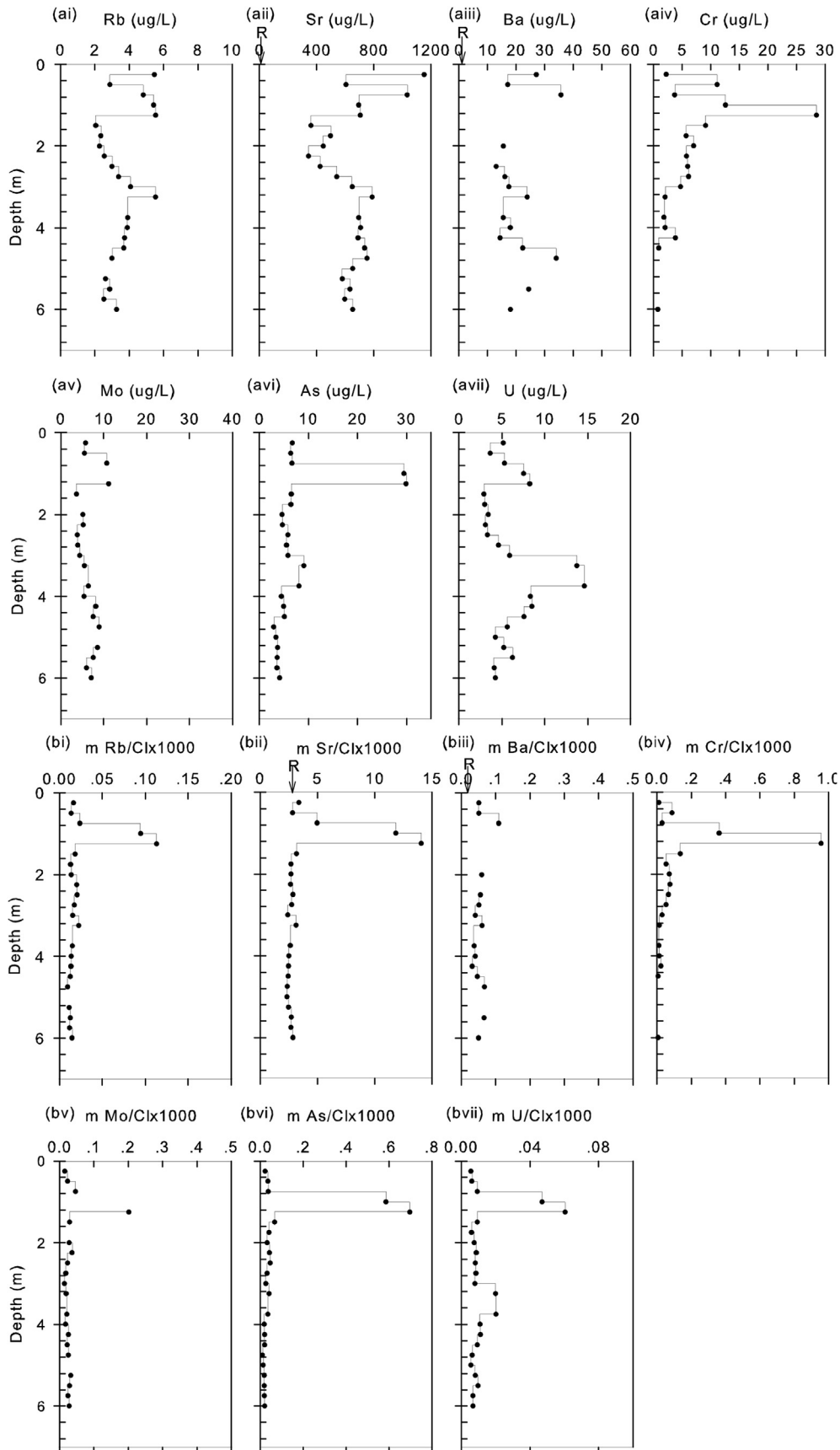


Fig. 9. Trace element concentrations of SS profile (ai to avii); b) Trace element to Cl molar ratios of SS profile (bi to bvii). Symbol R indicates rainfall elemental concentrations and its molar ratios to Cl.

1985).

In profile BA, both Sr and Ba concentrations start low, and there is a subsurface peak at around 1.5 m depth that decreases back to near-surface levels (Fig. 8 aii and aiii), and this peak coincides with trends in Ca and Mg cation concentrations (Fig. 5 aiii and aiv). BA profile is the only one to reach the water table and both Ba and Sr show marked increases in the capillary zone, which suggests a further reactive environment within the zone of (present or past) groundwater table fluctuation. At the water table a strong concentration (relative to Cl) decrease is observed coincident with mixing with the regional groundwater body (Fig. 8 bii and biii).

The other trace elements in profile BA include Cr, As and U with the exception of Mo, which are subject to redox controls and are mobilized under oxidizing conditions in oxyanion form. Whilst direct measurement of redox potential (Eh) or dissolved oxygen were not possible, the presence of an oxidizing environment is indicated by universally high NO₃ concentrations and low Fe concentrations (Fig. 3 aiii, Fig. 4 aiii and Table 2). Chromium shows oscillating values in the USZ (average for 8.9 µg/l) but with no enrichment in the capillary zone (Fig. 8 aiv). There are however lower values (2.5 µg/l) in the underlying regional aquifer (Table 2). Arsenic like Cr shows that reaction occurs in the USZ leading to a mean value of 7.7 µg/l, but with no enrichment in the capillary zone suggesting lower concentrations in regional groundwater (Fig. 8 avi). Uranium concentrations average 1.7 µg/l in the USZ and show significant enrichment in the capillary zone approaching 17 µg/l (Fig. 8 avii). Lower values (1 µg/l) of U are found in the regional aquifer (Table 2). By comparing with Cl (mU/Cl ratios) there is also a distinct enrichment taking place at the capillary zone (Fig. 8 bvii). Mo is like U with an average concentration of 8.7 µg/l in the USZ of BA profile (Fig. 8 av). The enriched Mo concentration reached 37 µg/l in the capillary zone (Fig. 8 av). However, the regional groundwater has Mo concentration of 5 µg/l which also indicates a distinct enrichment at the capillary zone (Table 2).

A similar set of results is observed for SS profile (Fig. 9), although the relationship to the water table cannot be studied. The mean concentrations for the USZ for the main set of trace metals are shown in Table 2. Comparable concentrations for the metals are found with BA profile, but with U being higher in the USZ of profile SS (Table 2 and Fig. 9 avii). Comparing to Cl, most trace elements show a constant or very slightly progressive increase with depth to 2 m, suggesting that most reaction has taken place above 2 m (Fig. 9 bi to bvii) in the zone of fluctuation within the USZs.

In summary the metal concentrations are established rapidly in near-surface moisture and show some enrichment due to chemical reaction in the USZ profile. Trace elements are uniformly lower in the regional groundwater, whilst showing some net enrichment in the capillary zone (based on profile BA).

4. Discussion

This is the first study of pore water chemistry using directly extracted pore moisture from the USZ within an entirely pristine (unpolluted) arid region. Extraction of moisture directly from the USZ presents risks of contamination and artifacts associated with the low sample volumes. Occasional data points from samples with low yields has been omitted, yet there is sufficient information from the results available which can be validated by the similarity of sequential geochemical profiles with depth for all major anions and cations as well as some trace elements. These profiles combine information on inert chemical tracers with reconnaissance information on reactive tracers to improve understanding of geochemical processes that occur as rainfall moves through the soil via the USZ. In one of the two profiles (BA) this also includes interaction within the capillary zone at the water table. These geochemical

processes can be considered alongside recharge rates and hydrostratigraphies provided using CMB.

4.1. Recharge rates and Cl-chronology

The direct recharge to the aquifer through the USZ has been calculated using the CMB (EQ. 1) using a mean Cl concentration of 85.5 mg/l (below 1 m) for profile SS and a mean Cl concentration of 42.3 mg/l between 1 m and 4 m (above the capillary fringe) for profile BA. Average recharge rates for the BA and SS profiles are 3.0 and 1.5 mm/year, respectively. Notwithstanding uncertainties introduced by potential variations in long term rainfall amount and Cl concentrations the estimated recharge rates in these two profiles are consistent with other profiles in the same area (Ma and Edmunds, 2006; Gates et al., 2008b; Scanlon et al., 2010).

The Cl-chronology for the two profiles is calculated for the portion below the zero-flux plane (estimated at around 2 m at these locations). The BA profile corresponds to a timescales of 40 years and SS with lower inter-annual Cl corresponds to 90 years (Fig. 10). The time-calibrated USZ chemistry in pristine areas such as this can be considered as a potential archive of changing atmospheric inputs using inert tracers. For example tritium has been used as an indicator of anthropogenic contamination as well as a recharge indicator (Robertson and Cherry, 1989). In the present case SO₄ might be of interest as a recorder of changes in aerosol deposition over the past century (Fig. 11). Assuming SO₄ behaves conservatively under the oxidizing environment, then the higher SO₄/Cl since 1995 may be providing a record of higher industrial activity and sulphur emissions.

4.2. Source of dissolved nitrate

High NO₃ concentrations in the USZ are found widely in other arid and semi-arid areas including western United States (Walvoord et al., 2003), the Sahel in northern Africa (Edmunds and Gaye, 1997; Deans et al., 2005), the Kalahari desert in southern Africa (Heaton et al., 1983; Stone and Edmunds, 2014), Australia (Barnes et al., 1992) as well as China (Gates et al., 2008c). In these areas, as in the present study, aerobic conditions permit the inert behaviour and preservation of biogenically produced NO₃. The NO₃ enrichment in the USZ is also consistent with the findings within other parts of the Badain Jaran by Gates et al., 2008c. Explanations for the enrichment are widely related to biogeochemical production in the soil zone either by N-fixation by leguminous plants or by cyanobacteria. The lack of macro-vegetation in the Badain Jaran desert probably limits significant biological N-fixation, although limited vegetation is to be found. At least 55 N-fixing leguminous

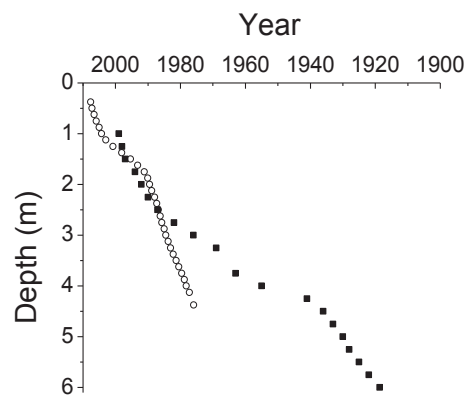


Fig. 10. Chloride-chronology calculated from cumulative chloride concentrations using EQ2 (BA open symbols and SS solid symbols).

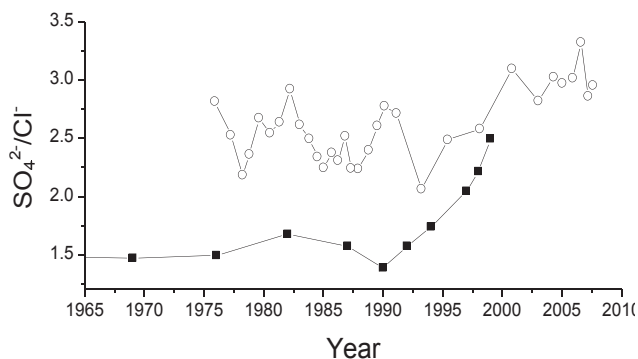


Fig. 11. SO₄/Cl change over time for BA (open symbols) and SS (solid symbols) profiles.

vegetation species have been documented in the Alashan Plateau (Wang and Hu, 2001), and salt and aridity-tolerant cyanobacteria are capable of subsisting at the dune surface (Warren-Rhodes et al., 2007). Anthropogenic inputs to the USZ or groundwater in the pristine Badain Jaran area can be excluded as a source of NO₃. One local source could be laminae of lacustrine sediments containing organic matter, interbedded in the overall well-sorted fine sands, which can be oxidized to NO₃. Unaccounted atmospheric N inputs such as NH₃ is another potential source of nitrogen (Gates et al., 2008c), raising baseline values. In the profiles obtained from the present study, whilst a biogenic origin for the NO₃ seems likely, the control (N-fixation or cyanobacteria) and release mechanisms cannot be confirmed without further investigation.

4.3. Water-rock interaction

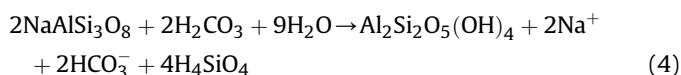
The profile results indicate that hydrological and geochemical processes are intense right from the surface. The zone of fluctuation to a depth of 2 m is where the evaporative Cl signal is established, from which recharge estimates are calculated from the concentration moving from this horizon. The main chemical characteristics of the groundwater are also determined in this zone. Inert tracers such as Cl are concentrated by purely physical processes, but reactive tracers (eg cations) all increase significantly relative to rainfall Cl.

The results show very clearly that water-rock interaction takes place right from the top of the profile and that there is then relatively little change in the hydrochemistry below the zone of fluctuation. This is a non-carbonate aquifer in the stratigraphical sense although carbonate mineral (and other mineral) saturation and formation may occur due to the changing water-rock ratios caused by cyclic evaporation processes.

The gain in solutes in the shallowest horizons, shown earlier, can be clearly related to the weathering reactions of silicate minerals (Garrels and Mackenzie, 1967) of which the predominant are likely to be feldspars; quartz is likely to be relatively stable except at pH above 9.0 (Langmuir, 1997). The weathering of albite can be written:



Or



This shows that this is an acid consuming hydrolysis reaction which may proceed at low pH (below 4.5) by reaction with “acidic” rainfall, or, most commonly under circumneutral conditions (Table 1) and in the presence of CO₂ (carbonic acid in Eqs (3) and (4)) to produce bicarbonate alkalinity. In totally abiotic environments with only rainfall inputs and under open system conditions this reaction will be slow due to low pCO₂ availability, but soil biological CO₂ may increase pCO₂ by one order of magnitude with consequent acceleration of reactions.

It is clear from the profile chemistry (BA and SS) that the rapid reactions are taking place and it may be inferred that biogenic soil CO₂ production is facilitating the reactions. Thus, rapid reaction of feldspars would account for the pore water Na and Ca increases and the production of the Si (H₄SiO₄).

In the absence of direct measurement of DO and Eh, it may be inferred that the USZ is an aerobic environment from high concentrations of NO₃ and also several oxyanions (U, Cr, Mo) and low levels of Fe. This enrichment also implies a trace element source from water-rock interaction with minerals in the profile.

4.4. Regional aquifer and the capillary zone

Profile BA shows the transition between the modern water, taking some 40 years to reach the water table and the regional aquifer which has an age of approximately 1–2 ka (Gates et al., 2008d). There is a discontinuity as shown by Cl and several other elements. The capillary zone extends over 2 m (Fig. 2) over which interval there is a capillary rise of older water (shown clearly by Cl). Some of the element plots vs Cl suggest that the upper part of the capillary zone is a zone of increased geochemical reaction (locally higher mMg/Cl, mF/Cl and some trace elements e.g. Ba, Sr, U, Mo). This could correlate with and be driven by seasonal oscillations in the regional water table and lake levels.

5. Conclusions

The direct use of pore waters obtained by immiscible liquid displacement in the study of the USZ unlocks new possibilities for geochemical and environmental research. Improvements in analytical technique and analytical detection limits should enable more detailed analysis in the future, although the limitation will be set by the practical constraint of handling and extracting small sample volumes. Importantly the USZ provides a temporal record of potential environmental change. Whilst this study is located in a pristine environment, in other locations impacts such as land use change could be investigated using this approach.

A full investigation of the water-rock interaction requires parallel study of the mineralogy which was not possible here. Additional measurements such as microanalysis of stable isotopes (δ¹⁸O, δ²H) would allow a closer examination of the moisture movement, recharge processes and definition of the zero flux plane.

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